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铜基催化剂在电催化析氢中的研究进展

郭　妍，李海双，王丽丽，马青华，赵　丽*

兰州交通大学化学化工学院，甘肃　兰州

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摘　要

在全球能源结构转型背景下，化石燃料的过度消耗导致温室气体排放激增与环境污染加剧，而传统贵金属催化剂(如Pt基材料)受限于高昂成本与资源稀缺性，难以满足规模化电解水制氢需求。鉴于此，研发兼具高催化活性与长循环稳定性的非贵金属基催化剂，已成为突破电解水析氢反应(HER)技术瓶颈的核心方向。Cu基催化剂因其天然丰度高、导电性优异及电子结构可调性强等优势，展现出替代贵金属催化剂的巨大潜力。本文系统梳理近年来铜基电催化剂在HER领域的研究进展，重点解析其纳米结构设计、合金化改性及界面工程等关键策略对催化性能的调控机制，并探讨规模化应用面临的挑战。该研究不仅为降低电解水制氢能耗提供理论支撑，更为构建清洁低碳能源体系与加速实现“双碳”战略目标提供双重技术路径。

关键词

非贵金属，Cu基电催化剂，析氢反应

Progress of Copper-Based Catalysts in Electrocatalytic Hydrogen Precipitation

Yan Guo, Haishuang Li, Lili Wang, Qinghua Ma, Li Zhao*

College of Chemistry and Chemical Engineering, Lanzhou Jiaotong University, Lanzhou Gansu

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Abstract

In the context of the global energy transition, the overconsumption of fossil fuels has led to a surge in greenhouse gas emissions and increased environmental pollution, while traditional noble metal catalysts (e.g., Pt-based materials) are difficult to meet the demand for large-scale hydrogen

*通讯作者。

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electrolysis (HER) due to their high cost and scarcity of resources. In view of this, the development of non-precious metal-based catalysts with high catalytic activity and long cycle stability has become a core direction to break the bottleneck of hydrogen electrolysis reaction (HER), and Cu-based catalysts have shown great potential for replacing precious metal catalysts due to their high natural abundance, excellent electrical conductivity, and tunable electronic structure, etc. In this paper, we systematically review the recent development of Cu-based catalysts for HER. In this paper, we systematically review the research progress of Cu-based electrocatalysts in the field of HER in recent years, focusing on the regulation mechanism of catalytic performance by key strategies such as nanostructural design, alloying modification and interfacial engineering, as well as discussing the challenges of large-scale application. This study not only provides theoretical support for reducing the energy consumption of hydrogen production from electrolytic water, but also provides a dual technology path for building a clean and low-carbon energy system and accelerating the realisation of the "dual-carbon" strategic goal.

Keywords

Non-Precious Metals, Cu-Based Electrocatalysts, Hydrogen Precipitation Reaction

1. 引言

全球能源需求激增和化石燃料过度消耗导致温室效应加剧，发展清洁、可再生的替代能源已成为实现“碳中和”目标的迫切需求。氢能因其高能量密度(142 MJ/kg)、零碳排放和广泛的应用场景(如氢燃料电池、工业脱碳和可再生能源储能)，被视为未来能源体系的核心载体之一[1]。然而，目前约 95%的氢气(H2)仍通过化石燃料重整制备，其过程伴随着大量二氧化碳(CO2)排放。通过可再生能源(如风电、光伏)驱动的电催化水分解技术制备“绿氢”，是解决这一矛盾的关键路径[2]。

作为水分解的半反应之一，析氢反应(HER)需要克服其缓慢的动力学过程，这往往需要施加较大的电压，从而导致能量的过度消耗[3]-[7]。为了降低这种过度消耗，开发高效的 HER 电催化剂至关重要。当前，HER 的核心挑战在于开发高效、稳定且低成本的催化剂。铂(Pt)基催化剂因其近乎理想的氢吸附自由能($\Delta G_{H^*} \approx 0$)被公认为是最佳的 HER 催化剂，但由于稀缺的资源和高昂的成本严重制约了其的规模化应用[8]。非贵金属催化剂(如过渡金属硫化物[9]、磷化物[10]、单原子催化剂[11])可通过调控电子结构、界面工程和载体协同效应，实现与 Pt 相媲美的催化性能。然而，非贵金属催化剂仍面临活性位点暴露不足、反应动力学缓慢及稳定性差等挑战，这使它的 HER 性能无法进一步提升。电催化析氢是电解水的阴极反应，在施加电压的条件下 H_2O 分别在电极的阴极和阳极发生还原反应和氧化反应而生成 H_2 和氧气(O_2)(图 1)。阴极表面质子被还原发生 HER 生成 H_2，与此同时阳极表面发生水氧化反应(Oxygen Evolution Reaction，简称 OER)生成 O_2，H_2 和 O_2 其摩尔比为 2:1 [12]。但是由于纯水在常温条件下电导率较低(5.5×10^{-6} S/m)，电离产生的氢离子(H^+)和氢氧根离子(OH^-)浓度极低(10^{-7} mol/L)，无法形成有效的离子传输通道。为了实现有效的离子传递一般在水中加入强电解质，如强酸、强碱以及中性溶液以提高电解液的电导率。此外，电解质的加入还改变了水的 pH 值，优化了反应的动力学，在不同的电解质溶液中，水在阴极和阳极催化剂表面的电化学反应也发生变化。

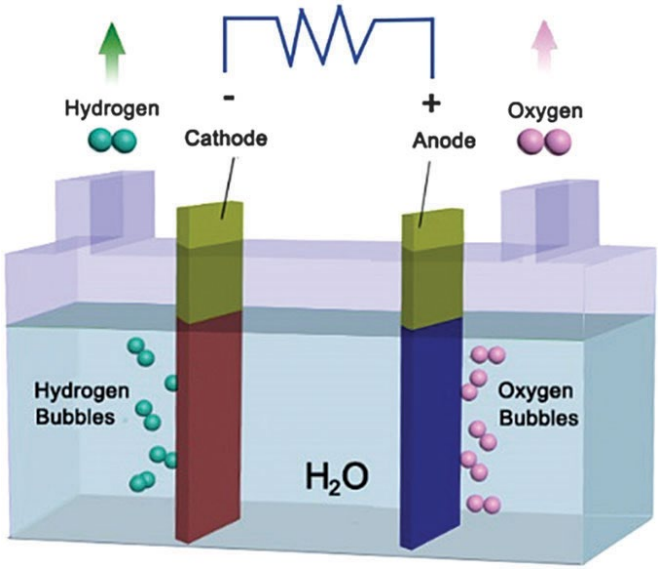

Figure 1. Schematic diagram of a water electrolysis unit [13]
图 1. 电解水装置示意图[13]

为了寻找贵金属催化剂的替代品，近年来许多研究致力于开发非贵金属催化剂体系。铜(Cu)、钴(Co)、镍(Ni)、铁(Fe)等非贵金属基过渡金属化合物，因其具有可调控的电子构型及多活性位点特性，在电催化、能源存储等领域备受关注。通过晶格掺杂、缺陷工程等策略，可精准调控其费米能级附近的态密度分布，进而优化表面反应动力学路径[14]-[18]。以 Cu 为例，研究表明其界面 H*吸附能垒相较于 Ni 更接近 HER 的动力学需求[19]，展现出其在高效催化 HER 过程中的显著优势。

2. Cu 基催化剂的改性策略

Cu 基催化剂的合成方法主要包括：溶胶－凝胶法、电化学沉积法、水热/溶剂热法、模板法、前驱体的固态热转化法等。这些技术主要可以归分为两类：自下而上法和自上而下法。自下而上的方法通过原子、分子或纳米单元的自组装或化学反应，逐步构建出目标材料或结构，实现材料的可控生长。而自上而下的方法通过物理或化学手段将大块材料逐步分解、裁剪或刻蚀，获得具有特定尺寸和形貌的纳米或微米结构[20]。

由于贵金属材料储量稀少、成本高，这限制了其在电解水领域的规模化应用。目前，贵金属催化剂的研究主要集中在如何减少贵金属含量、提高其稳定性等两个方向。为了优化 HER 的催化剂，克服贵金属材料的不足，目前提出来一些对贵金属基材料及其氧化物的改进策略，包括：掺杂工程、缺陷工程、表面/界面工程。

2.1. 掺杂

对于氧化还原反应，其本质是电子的转移和得失，因此催化剂本身必须具有优异的电子传导性能。掺杂策略是一种通过引入具有优异化学性能的元素和具有构建良好电子传导的微界面来改变催化反应的有效方法[21]。掺杂可分为金属原子掺杂[22]-[25]和非金属原子掺杂[26]-[28]或多原子共掺杂[29]-[32]。金属掺杂是当今相对常见的方法，贵金属可以掺杂到过渡金属氧化物中以制备贵金属氧化物。利用掺杂策略可优化催化剂的电子结构，增强催化活性，通过非金属掺杂可以暴露更多活性位点。但掺杂过程中的均一性难以控制，易形成团聚，导致性能不稳定。

2.2. 缺陷工程

缺陷工程对催化剂的物理和化学性质有较大的影响，通过精准调控金属氧化物的缺陷结构，可有效优化其表面/界面微观构型与电荷分布的特性，从而显著提升材料的本征催化活性及稳定性。从物理结构的角度来看，缺陷工程增加了催化剂的有效电化学活性面积，并提供了更多的催化活性位点。从催化反应过程的角度来看，缺陷的形成影响催化反应的方向和速率。目前已被广泛应用于对催化剂的有效改进，并在各种化学合成和转化领域取得了重大进展[33]。常见的缺陷包括空位缺陷[34]、官能团缺陷[35]、掺杂缺陷[36]、边缘缺陷等。目前常用于制造缺陷的方法如图 2 所示。由于部分缺陷易在反应条件下重构或消失，且当缺陷浓度过高可能导致结构坍塌或电子散射，因此缺陷工程存在稳定性和可控性的挑战。

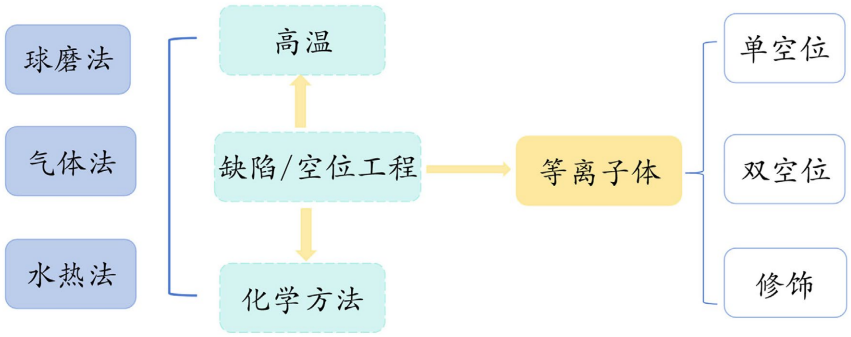

Figure 2. Schematic diagram of defect/vacancy works
图 2. 缺陷/空缺工程示意图

2.3. 表面/界面工程

常见的界面包括催化剂与相互作用分子之间的界面、催化金属与载体之间的界面以及由特殊结构形成的界面，如核壳与晶体晶面之间的界面。界面和表面的催化工程设计如图 3 所示[21]。大多数情况通过构建异质结来实现界面工程，异质结可分为半导体－半导体异质结(包括 I 型、II 型、III 型、p-n 和 Z 型)和半导体－金属异质结(包含肖特基结和欧姆结) [37] [38]。在异质结界面有利于电极表面上的电子转移反应，显著促进整个多步基元反应的反应动力学，降低热力学能垒，从而提高电催化剂的性能。但异质结结构的制备复杂度高，需精确控制界面组成与形貌。

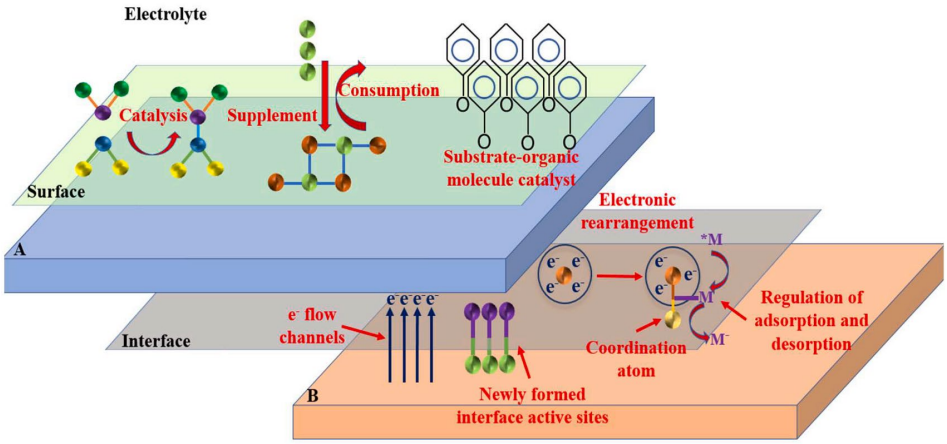

Figure 3. Schematic diagram of interface/surface engineering [21]
图 3. 界面/表面工程示意图[21]

三种策略通过调控电子结构、缺陷分布及界面特性来提升 HER 性能。三种策略相辅相成：掺杂可诱导缺陷生成，缺陷富集的界面则强化异质结协同效应，但需权衡合成过程的复杂度与性能的提升量。通过多策略协同设计及绿色合成技术，可以有效平衡催化剂的活性、稳定性与成本，推动高效 HER 催化剂的实际发展，是目前突破贵金属催化剂瓶颈的关键路径。

3. Cu 基催化剂的在 HER 领域的研究进展

Cu 基催化剂及其复合物由于具备低廉的成本、丰富的含量、高的导电性、和优异的催化活性，在催化领域具有广泛的应用前景。目前大多数 Cu 基催化剂被用于电催化 CO_2 还原、氧还原反应、以及电催化析氢等。虽然贵金属 Pt、Ru 材料在电催化 HER 中具有优异的催化活性，但成本较高，且稳定性较差。目前大多数研究致力于采用过渡金属催化剂来代替贵金属催化剂，以降低反应成本。根据 ΔG_{H^*}与 j_0 的火山关系图来看(图 4)，过渡金属 Cu 基催化剂的 $\Delta G_{H^*} > 0$，较高的 ΔG_{H^*}使得催化位点对氢吸附能力减弱，理论上来说 Cu 基材料不是理想的电催化 HER 的催化剂。但 CuO 在碱性条件下表现出优异的电化学活性和化学稳定性，可在长时间电解过程中保持结构完整性，不易被腐蚀。通过与其他材料复合(如 CuO/MoS_2、CuO/rGO)，可在中性或酸性条件下电解水，以此来满足不同电解体系需求。

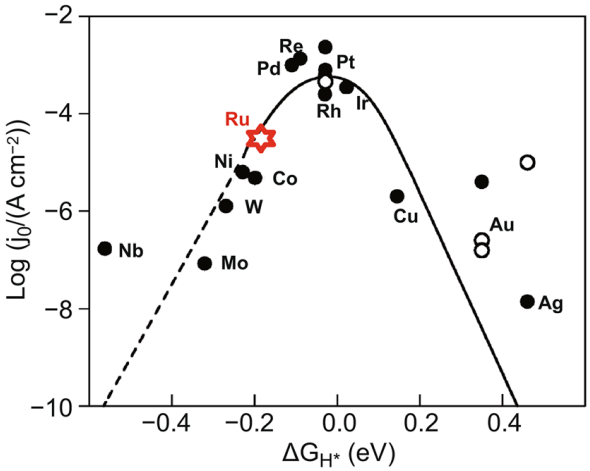

Figure 4. Volcano plot of ΔGH* for different metal catalysts in HER [39]
图 4. 不同金属催化剂在 HER 中的 ΔGH*的火山图[39]

Paul 等人[40]使用水热法制备了 $Cu_2O/g\text{-}C_3N_4$ 纳米复合材料，并探究材料在碱性条件下的电化学析氢性能，结果表明，材料的过电位为 148.7 mV 且 Tafel 斜率明显较低，为 55 mV dec^{-1}。研究发现石墨氮化碳的掺入导致 Cu_2O 的电化学活性面积增大，反应动力学加快。Wang 等人[41]通过使用双模板组装法开发了一种新型的 Cu 基电催化剂($RuCuO_x$/NC)。使用传统的三电极体系在 1 M KOH 中测试了 RuCu 基复合材料对 HER 的电催化效果，发现 $RuCuO_x$/NC 在 10 mA cm^{-2} 的电流密度下，过电位低至 29 mV，Tafel 斜率也较低为 57.7 mV dec^{-1}。对于碱性 HER，$RuCuO_x$/NC 的性能优于之前所报道的其他电催化剂。该研究为 Cu 基电催化剂的设计提供了一种创新策略：通过微量贵金属掺杂可显著提升过渡金属催化剂的 HER 活性。该策略突破了传统非贵金属催化剂活性位点受限的瓶颈，为开发高效稳定的低成本电解水催化剂开辟了新方向。Geng 等人[42]，采用溶剂热法在导电性好的碳布上生长邻苯二酚铜纳米棒阵列(CuCo-CAT/CC)作为 HER 的电催化剂，材料在碱性和中性溶液中表现出优异的 HER 性能，在 10 mA cm^{-2} 的电流密度下分别具有 52 和 143 mV 的低过电位，优于大多数非贵金属基催化剂。此外，MOF 纳米棒阵列在碳布基底上的原位生长不仅使材料具有开放的多孔互连结构，而且避免了使用任何粘合剂，从而使 HER

在碱性和中性电解质中具有强大的稳定性。

4. 结论

HER 作为水电解制氢的核心半反应，在实现“双碳”战略目标和构建清洁能源体系中具有重大意义。目前，贵金属 Pt 基催化剂虽具有优异的 HER 活性，但其含量稀缺与成本高昂严重制约了电解水制氢技术的商业化进程。因此，开发兼具高催化活性、长期稳定性和低成本效益的非贵金属催化剂材料，成为突破氢能产业瓶颈的关键科学问题。众所周知，近年来，Cu 基电催化剂在 HER 领域取得了突破性进展，通过结构调控、组分优化及机理探索，显著提升了其催化活性和稳定性，展现出替代贵金属催化剂的潜力。铜基催化剂的快速发展为高效、低成本电解水制氢提供了重要技术路径，但其工业化应用仍需在材料稳定性、规模化生产及多场景适应性方面进一步突破。未来研究应聚焦多学科交叉，结合实验与计算模拟，推动铜基催化剂从实验室迈向实际应用，助力全球碳中和目标的实现。

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